Environmental Science Program at the Advanced Light Source FY06 Annual Report

Project Team: Peter Nico, Susan Hubbard, David Shuh (LBNL)

Research Objective

The goal of the ERSP Environmental Science Program at the Advanced Light Source (ALS) is to further the research mission of OBER's Environmental Remediation Science Program (ERSP) program by improving utilization of the ALS. The ALS is a DOE national user facility with many unique spectroscopic and microscopic capabilities suited to application in research areas of interest to ERSP. The program supports the research mission of ERSP by supporting ERSP PIs on research projects that can benefit from the resources at the ALS. These collaborations take many different forms including participation in experimental design, novel sample cell development, data interpretation, beam time proposal writing, and data collection. The program is especially committed to improving the environmental relevance of measurements made at the ALS by working with ERSP PIs to design and build experimental equipment that allow for novel in situ measurements. Frequently, it is no longer sufficient to bring a series of samples from the field to the ALS. For the most innovated investigations, one must bring the field environment to the light source in as faithful a manner as possible. The program specifically focuses on four beam lines at the ALS which were identified through consultations with ERSP investigators as being of the most interest to the environmental science community. These beam lines include, BL 1.4.3-Infrared spectromicroscopy, BL 8.3.2-X-ray micro-tomography, BL 10.3.2-X-ray fluorescence, micro-X-ray absorption spectroscopy, and micro-X-ray diffraction, and BL 11.0.2-Scanning Transmission X-ray Microscopy (STXM) and Ambient Pressure Photoemission Spectroscopy (APPES). Research developments and progress toward the program goals are discussed below.

Research Progress and Implications

This report summarizes progress as of the second year of a four year program. Dr. Peter Nico, the program lead, was hired near the end of year one; the accomplishments described herein represent approximately one year of full time activity. This activity includes basic support and outreach components, as well as research assistance to ERSP investigators. Described below are some research highlights from the past year associated with the ALS program. A list of other ERSP/BER investigators that have also been supported by the program in various ways is included as Additional Information. The program has advanced several projects investigating biomineralization processes using all four of the core environmental beam lines. For example, the ALS program has worked with the Fendorf group (Stanford University) to use the capabilities of beam line 10.3.2 to map the distribution of microbial colonies on the surface of an Oak Ridge soil aggregate by labeling the bacteria with CdSe quantum dots and using the X-ray fluorescence capabilities of 10.3.2 to locate the Cd and Se fluorescence signals. Once the bacteria were located, micro-X-ray absorption data was collected from different locations underneath and away from the microbial colonies to identify differences in the chemistry of the underlying mineral. Figure 1 shows that the Fe mineralogy away from the microbial communities appears to be more reduced, magnetite like, than the Fe underneath the colony. Since most of the Fe was initially oxidized, this observation implies that microbial colonies are sensitive to Fe mineral changes and are constantly moving to the most easily metabolized mineral regions.

A related project has focused on the development of a flow cell bioreactor suitable for using synchrotron Infrared Spectroscopy (BL 1.4.3) to examine Fe mineral transformation in an anaerobic, hydrated system, with undisturbed microbial colonies. Synchrotron IR is unique in its ability to provide chemical information with micron scale spatial resolution while not altering the metabolism of the bacteria in the system. By collaboration with the Geesey group (Montana State University), we have designed and built a new microbial bioreactor. The new reactor uses CVD diamond windows to allow for transmission of both IR light and visible light (used to directly image the bacteria) while being chemical inert and gas impermeable (Figure 2A). The lower window of the cell can be raised or lowered to control the water layer thickness with in the cell. This is crucial due to the strong IR absorbing nature of water. To begin the experiment, the lower window of the sample chamber was coated with a hematite film using PNNL/EMSL facilities. Figure 2B,C shows a visible image of the hematite film along an infrared chemical map showing the location of the bacterial colonies on that film. Early results have shown increased disorder in the hematite structure due to hydration and/or metabolic action of the bacteria. While new secondary Fe minerals have not been seen in this system, we have observed IR spectra which may be indicative of Fe(II) bound to extra cellular polysaccharides or cell membrane components. This observation would be consistent with previous investigations while providing

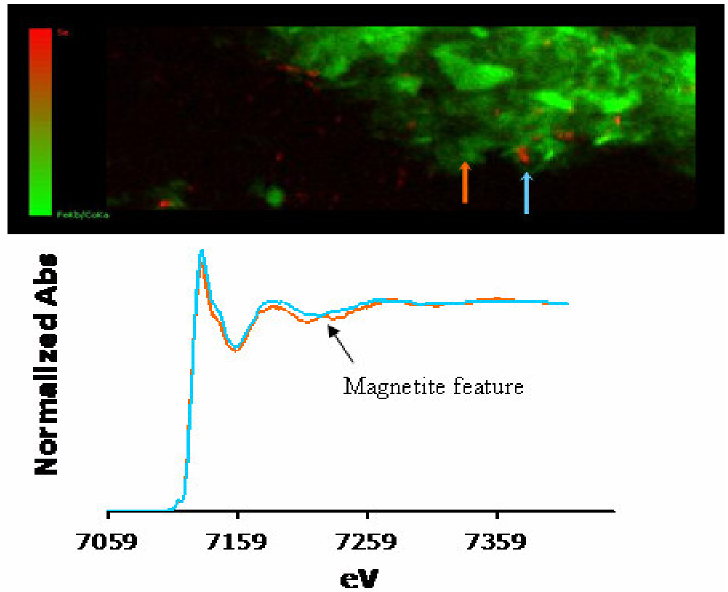


Figure 1: Fe is shown in green and microbial colonies are shown in red. The XANES spectrum from away colonies appears to have a signal characteristic of magnetite which is lacking in the near spectrum.

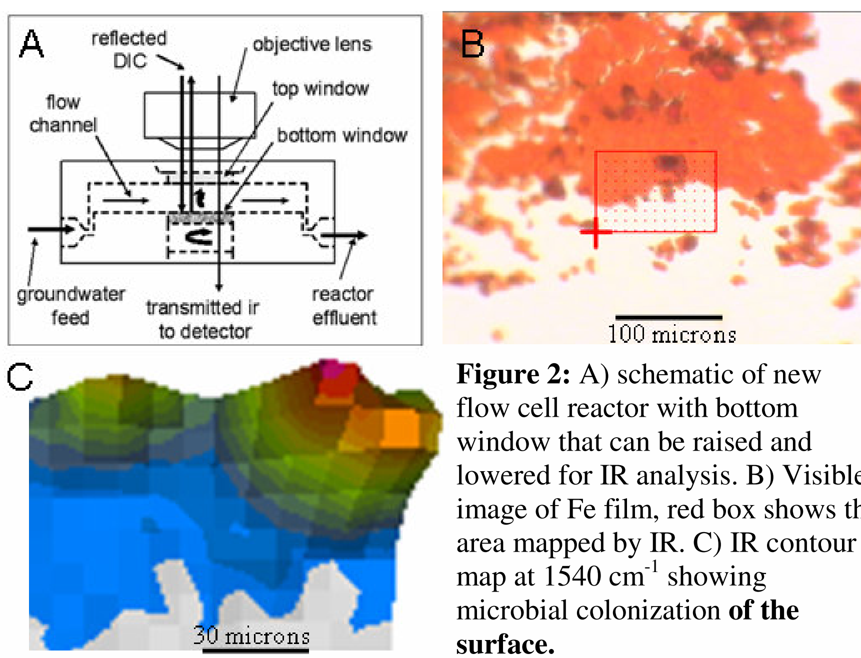
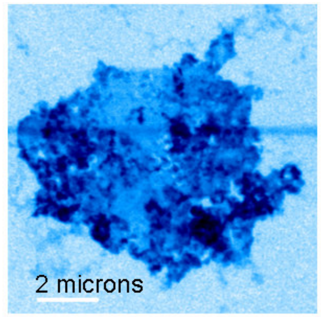
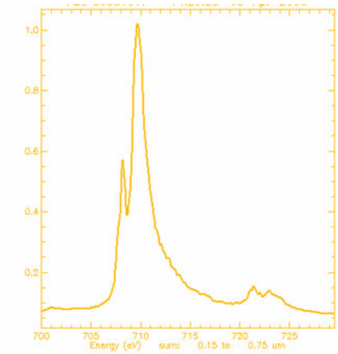


Figure 2: A) schematic of new flow cell reactor with bottom window that can be raised and lowered for IR analysis. B) Visible image of Fe film, red box shows the area mapped by IR. C) IR contour map at 1540 cm^{-1} showing microbial colonization **of the surface.**

the first direct spectroscopic observation of the phenomenon in an actively metabolizing system. This advance in experimental technology has generated much interest from other ERSP investigators and planning for additional experiments is currently underway.

Our program has also assisted the Steefel group (LBNL), who are developing beam line flow cell technology. Using STXM (BL 11.0.2), this project has used flow cell technology to investigate Fe mineral transformation with nanometer scale spatial resolution. The program helped to support the acquisition of STXM data using their newly designed cell. An example of the type of data collected is shown in Figure 3.





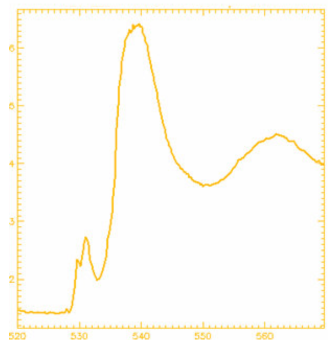


Figure 3: A) image of Fe particle from flow cell after reaction with AH_2DS. B) NEXAFS iron spectrum taken from particle. C) NEXAFS oxygen spectrum taken from particle.

A final example of research advanced by the program comes from the Hubbard and Banfield groups. In this case the three dimensional imaging capabilities of beam line 8.3.2 were used to probe pore space changes in a packed quartz sand column during active SO_4^{2-} reduction in the presence of soluble Fe. The left image in Figure 4 is of quartz sand grains before sulfate reduction. The grain surfaces are rounded and the density of the grains as shown by brightness is uniform. The right image shows the same location after sulfate reduction. The grain surfaces and resulting pore spaces are now much more angular and irregular in shape due to the presence of a high density (as indicated by brightness) precipitate. This precipitate, presumably Fe sulfide, has altered the size and shape of the pore space within the column, which in turn will affect the flow dynamics and future nutrient and contaminant transport. BL 8.3.2 was off line for much of this year for upgrades. Thus, future

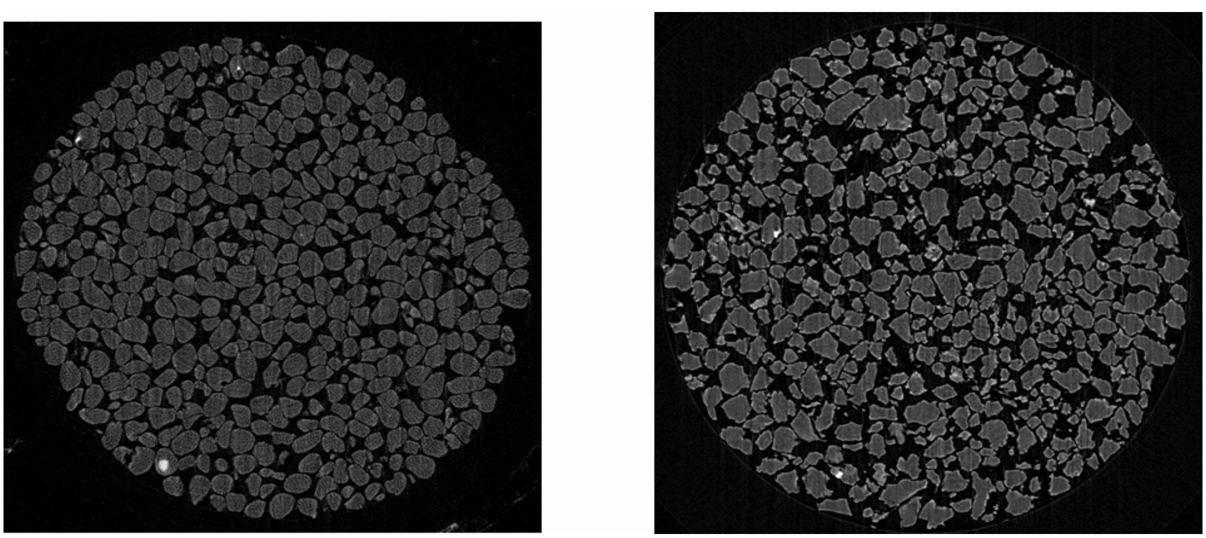


Figure 4: Left image shows quartz sand grains before sulfate reduction. Right image shows same location after sulfate reduction.

progress on this work has been delayed. However, the initial results are very promising.

In addition to the direct research advances supported through this program, as part of ERSP's expertise presence at the four different national light sources, the programs help ERSP investigators to make the best use of resources across the nation. For example, Dr. Barak Yorum of the Matin group (Stanford University) approached the ALS program regarding a need for chemical speciation of Cr and wondering whether XANES would be a suitable method for providing the necessary information. The ALS does not have an appropriate beam line for the proposed investigation, but through consultation with Dr. Bruce Ravel (ANL), Dr. Paul Northrup (BNL), and Dr Sam Webb (SSRL) not only was the most appropriate facility identified (SSRL) but also some beam time was made available by Dr. Sam Webb for a preliminary investigation, while Dr. Bruce Ravel and Dr. Paul Northrup contributed suggestions to the design of the initial experiment. Similarly, the program has been working with the FRC (ORNL) and the Kemner group (ANL) to coordinate the analysis of an FRC dolomite gravel sample with a distinct U coating between the ALS and the APS. The design of the APS makes it ideal for investigation of the U chemistry within the sample, but it is unable to probe the chemistry of the lighter elements such as O, Al, Ca, Si, and C. However, the STXM (BL 11.0.2) at the ALS is perfectly suited to investigate the chemistry of these elements. Therefore, through the ERSP light source programs synergy between the capabilities of the respective light sources is being achieved to the significant benefit of ERSP investigations.

Planned Activities

New experiments with ERSP PIs are planned for all four program beam lines for the upcoming ALS user cycle. Additional activities planned for the next year include preparation of an ALS approved program (AP) across one or more of the four beam lines covered by the program. Such an AP will allow more consistent access to beam time for the PIs served by the program. Examples of specific experiments to be conducted in FY07 include experiments planned with the Fendorf group (Stanford) and the O'Day group (U.C. Merced) on the micro-tomography beam line. (8.3.2). Additional experiments using the new IR flow cell and beam line 1.4.3 with the Geesey group and the Fendorf group are also designed and have been awarded the appropriate beam time. The collaboration with the FRC and the Kemner group will continue on beam line 11.0.2 with the analysis of the FRC gravel. The program will also continue its outreach to the ERSP PI's through attendance of the spring ERSP PI meeting and updating the website. In addition, the laboratory facilities available to PIs in the program will continue to be improved through the acquisition (already ordered, but yet to arrive) of an anaerobic chamber that will be essential for users wishing to prepare anaerobic subsurface samples with or without bacteria immediately before investigation at the ALS.

Information Access

Environmental Science at the Advanced Light Source webpage: http://esd.lbl.gov/ALS_environmental/index.html\

Additional Information

The following is a partial list of environmental researchers supported by BER who utilized the facility in the past year and who received program assistance.

Drs. Hendrick Bluhm of LBNL (EMSI), Gordon Brown, Jr. of Stanford University (EMSP, EMSI), Anders Nilsson of Stanford University (EMSI) and co workers studying chemical and microbiological interactions at solid-aqueous solution interfaces in Earth's near-surface environment, where natural waters, natural organic matter, and biological organisms interact with natural solids and environmental contaminants. (Beamline 11.0.2)

Dr. Scott Fendorf of Stanford University (ERSP, EMSI) and co workers were studying coupled geochemical and hydrological processes governing the fate and transport of radionuclides and toxic metals beneath the Hanford tank farms. (Beamline 10.3.2)

Dr. Andrea Foster of the USGS (EMSI) and coworkers were studying Arsenic speciation in mine wastes and sorption onto mica grains. (Beamline 10.3.2)

Drs. A.J. Francis and Cleveland Dodge of BNL (EMSP, EMSI) and co workers were studying natural and biostimulated transformation of Pu in soils. (Beamline 11.0.2)

Drs. Terry Hazen and Hoi-Ying Holman (Genomics: GTL) used the facility to explore issues related to molecular mechanisms of microbial transformation of metal oxyanions and aromatic organic compounds as they relate to bioremediation. (Beam line 1.4.3)

Drs. Susan Hubbard (LBNL) and Jillian Banfield (UCB/LBNL) (NABIR, EMSP) used the facility to examine samples solid samples and how microbial community activity and geochemical reactions alters the pore spaces in the material. (Beam line 8.3.2)

Dr. Satish Myneni of Princeton University (EMSP, EMSI) and coworkers conducted studies on H-bonding in water, coordination chemistry of Al^{3+} in aqueous solutions and in amorphous precipitates, and on the functional group chemistry of bacteria surfaces. They also examined the functional groups of C, N, and O in siderophores and their metal complexes. (Beam lines 11.0.2, 10.3.2)

Dr. Mary Neu of LANL (EMSP, NABIR) and co workers were studying plutonium and neptunium speciation and mobility in soils and the subsurface. (Beam line 11.0.2)

Drs. Klaus Pecher, Don Baer, and Yuri Gorby and co workers of PNNL (**NABIR**). (Beamline 11.0.2)

Drs. David Shuh and Wayne Lukens of LBNL (EMSP) and co workers in support of their research program to investigate the fundamental chemistry of technetium. (Beam line 11.0.2)

Dr. Carl Steefel of LBNL (EMSP, EMSI) and coworkers were studying the rates and mechanisms of clay dissolution in order to remove the long standing discrepancies between experimental data and field simulations. (Beam line 11.0.2

Dr. Margeret Torn (BER) using the STXM to investigate the structure and association of natural organic mater with mineral particles in soils. (Beam line 11.0.2)

Dr. Glenn Waychunas of LBNL (EMSI) characterization of novel radionuclide complexing dedrimers. (Beam line 11.0.2)